

DETECTING CHANGE IN WATER QUALITY FROM IMPLEMENTATION OF LIMESTONE TREATMENT SYSTEMS IN A COAL-MINED WATERSHED, PENNSYLVANIA

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During 1996-97, a variety of limestone-based treatment systems were implemented to neutralize acidic mine drainage and reduce the transport of dissolved metals in the northern part of the Swatara Creek watershed, which drains a 43-mi² (112-km²) area in the Southern Anthracite Field upstream from Ravine, Pa. Since 1996, the current project has monitored water quality upstream and downstream of each treatment and at integrator sites on lower reaches of Swatara Creek. Continuous measurements of pH and specific conductance and periodic sampling for alkalinity, acidity, sulfate, and metals upstream and downstream of each treatment system show that (1) open limestone channels and limestone-sand dosing generally had negligible effects on water quality and (2) limestone diversion wells and limestone drains generally were effective at producing near-neutral pH and attenuating dissolved metals during baseflow but were less effective during stormflow conditions. Storm runoff in this area commonly is acidic, and, as streamflow volume increases during stormflow conditions, a smaller fraction of total flow is treated and (or) residence time in the treatment system is reduced.

Monitoring on the mainstem of Swatara Creek indicates watershed-scale effects owing primarily to changes in mining practices and secondarily to watershed-wide implementation of treatment systems. Most underground mines in the Swatara Creek Basin were abandoned before 1960 and are presently flooded. Drainage from these mines contributes substantially to baseflow in Swatara Creek. For Swatara Creek at Ravine, Pa., which is immediately downstream of the mined area, long-term data collected since 1959 indicate sulfate concentration declined from about 150 mg/L in 1959 to 75 mg/L in 1999; pH increased sharply from 3.5-4.4 (median ~4) to 4.6-7.0 (median ~6) after 1975. These trends resulted from a decline in pyrite oxidation and the onset of carbonate buffering. Because these long-term attenuation processes have had such a pronounced effect on water quality in Swatara Creek, the effects of recent implementation of limestone treatments are difficult to detect at a watershed scale. Nevertheless, during ecological surveys prior to 1991, no fish were found in Swatara Creek at Ravine. Only six species of fish were found in 1994 and 1996. However, increasing numbers of fish have been found annually since 1996. In 1999, 21 species of fish were documented.

The recent monitoring on the mainstem of Swatara Creek indicates the limestone treatments mitigate extreme fluctuations in pH during storm events; however, additional buffering capacity is needed to maintain near-neutral pH of Swatara Creek during large storm events. Concentration

of sulfate, specific conductance, and pH are inversely related to streamflow at Ravine, indicating dilution and acidification during stormflow. Declines in stream-water pH to values approaching 5.0 could result in the remobilization of adsorbed or precipitated metals associated with sediments; declines in pH below 5.0 could cause injury to aquatic organisms. Generally, to maintain stream pH during storms, additional or larger limestone diversion wells could be constructed to begin or increase alkalinity production as the stream stage rises and/or additional or larger limestone drains could be constructed to produce greater amounts of alkalinity and enhance the buffering capacity of baseflow.

Introduction

The Pennsylvania Anthracite region consists of four large coalfields within an area of about 3,400 mi² (8,850 km²) in the Appalachian Mountain Section of the Ridge and Valley Physiographic Province in eastern Pennsylvania (Wood et al. 1986; Berg et al. 1989; Way 2000). The coalfields are the sites of a series of parallel, moderately to deeply downwarped synclinoria. Most mines in the region were developed to access multiple coalbeds of the Llewellyn and Pottsville Formations of Pennsylvanian Age. In the Southern Anthracite Field, a total of 38 coalbeds with average thicknesses ranging from 1 to 11.5 ft (0.3 to 2.5 m) have been identified and mined to depths exceeding 3,280 ft (1,000 m) (Wood et al. 1968, 1986).

More than 150 years of mining in the Southern Anthracite Field has adversely affected surface-water and ground-water supplies (Growitz et al. 1985; Wood 1996; Brady et al. 1998; Way 2000). For example, losses of stream water to and contaminated drainage from abandoned anthracite mines within the upper 43 mi² (112 km²) of the 576-mi² (1,492-km²) Swatara Creek Basin degrade the aquatic ecosystem and impair uses of Swatara Creek to its mouth on the Susquehanna River 59 mi (95 km) downstream from the mined area (fig. 1). Consequently, the Swatara Creek Basin was designated a “high priority watershed” for reducing nonpoint-source pollution (Pennsylvania Department of Environmental Protection 1998). Current land use in the upper 43-mi² (112-km²) area, upstream from Ravine, Pa., is classified as 86.6 percent forested, 4.9 percent agricultural, and only 6.4 percent barren, mined (U.S. Geological Survey 2000). The land-use classification for this extensively mined area is misleading, however, because underground mines extend beneath much of the surface and “natural” reforestation conceals large tracts of unreclaimed spoil. Downstream from the mined area, forested and agricultural land uses predominate. For example, land use in the 116-mi² (300-km²) area of the Swatara Creek Basin upstream from Pine Grove (fig. 1), inclusive of the area above Ravine, is classified as 69.7 percent forested, 25.0 percent agricultural, and 2.4 percent barren, mined.

Although several surface and underground anthracite mines presently are active, most mines in the Swatara Creek Basin were abandoned before 1960 (McCarren et al. 1964; Stuart et al. 1967). Barren, steep banks of spoil and culm and fine coal debris in siltation basins are sources of sediment (suspended solids) and dissolved ions in water that infiltrates or runs off the surface during storms (e.g. Olyphant et al. 1991). The abandoned underground mines have flooded and have collapsed locally causing subsidence. Surface flow is diverted through subsidence pits, fractures, and mine openings to the underground mines where the water becomes contaminated (Skelly & Loy, Inc. 1987; Ladwig et al. 1984; Growitz et al. 1985; Wood 1996). In downstream reaches, the contaminated water resurges as “acidic” or “abandoned” mine drainage (AMD), contaminating Swatara Creek and its tributaries while contributing substantially to baseflow (Fishel 1988).

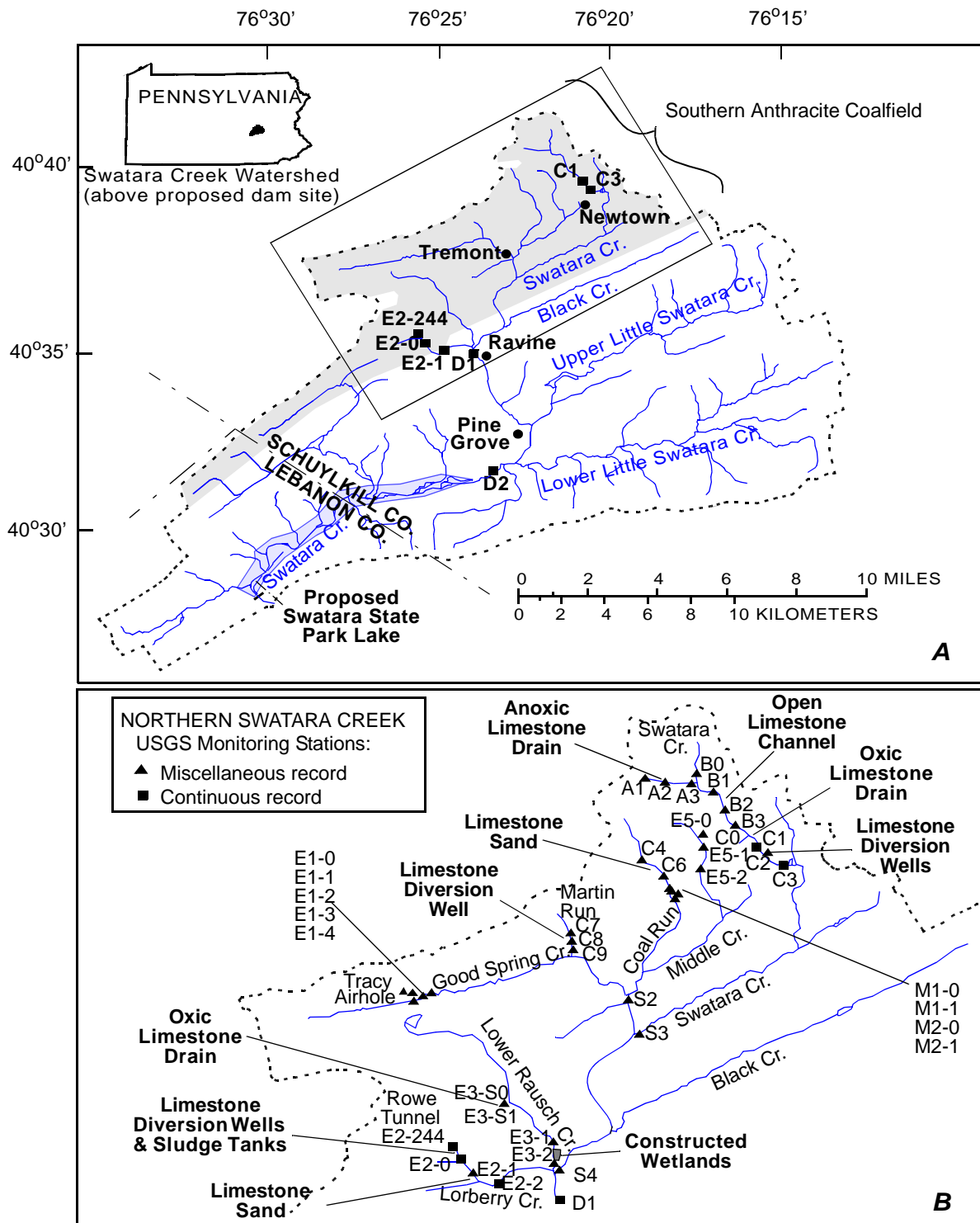
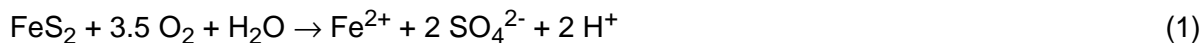


Figure 1. Locations of water-quality and streamflow monitoring sites in the Swatara Creek Basin, Lebanon and Schuylkill Counties, Pennsylvania: A, continuous monitoring sites on Swatara Creek above the proposed dam for Swatara State Park Reservoir; B, monitoring sites within the Southern Anthracite Coalfield, above Ravine (area denoted in A).

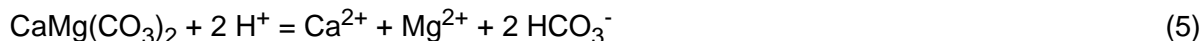
Coal-mine drainage commonly has elevated concentrations of sulfate (SO_4^{2-}), iron (Fe), manganese (Mn^{2+}), aluminum (Al^{3+}), and other solutes that result from the oxidation of pyrite (FeS_2) and the subsequent dissolution of carbonate, oxide, and aluminosilicate minerals by acidic water (Cravotta 1994; Rose and Cravotta 1998). Pyrite oxidation (reaction 1) takes place primarily in the unsaturated zone and at the land surface, where oxygen (O_2) and moisture are available and where acid (H^+) and other oxidation products tend to concentrate in fluids and solids.



Infiltrating water or surface runoff can dissolve and transport the acidic oxidation products. In contrast with SO_4^{2-} , which is transported primarily as a dissolved ion, Fe can be transported as ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions and as suspended Fe(III) solids (Cravotta 2000). In the presence of O_2 , Fe^{2+} tends to oxidize to Fe^{3+} (reaction 2) (Stumm and Morgan 1996). At pH >3, concentrations of Fe^{3+} are limited by the formation of Fe(III) oxyhydroxides and related solids (reaction 3) (Bigham et al. 1996).

The transport of dissolved Fe, Al, and trace metals typically is attenuated owing to precipitation and adsorption (Bigham et al. 1996; Smith et al. 1998; Webster et al. 1998; Cravotta and Trahan 1999). Attenuation generally is most effective as pH approaches neutrality (pH 6-7). However, at near-neutral pH and under anoxic conditions, concentrations of Fe^{2+} and Mn^{2+} can be elevated owing to relatively high solubility of Fe(II) and Mn(II) oxyhydroxides and carbonates. Aeration of water containing Fe^{2+} and Mn^{2+} can promote oxidation and hydrolysis, producing Fe(III) and Mn(III-IV) oxyhydroxides and 2 moles H^+ for each mole Fe^{2+} and Mn^{2+} . The potential for the production of H^+ (or consumption of OH^-) by hydrolysis reactions involving Fe, Mn, Al, and other metal ions is measured as acidity (Rose and Cravotta 1998).

The acid produced by pyrite oxidation or by hydrolysis can be neutralized by reaction with calcite (CaCO_3) and dolomite [$\text{CaMg}(\text{CO}_3)_2$].



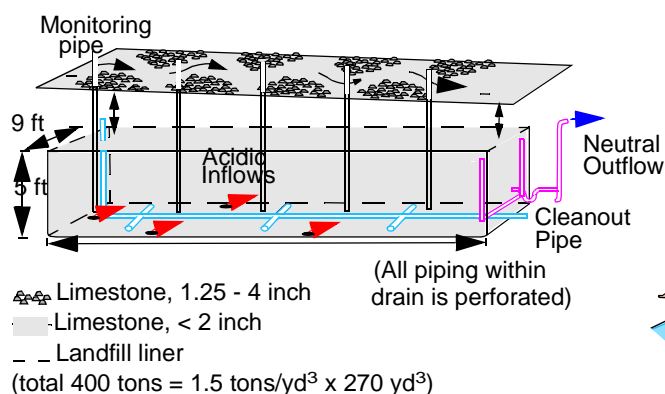
These calcareous minerals are the dominant components of limestone and can occur in nodules, cementing agents, or fractures in sandstone, siltstone, shale, and associated strata of coal-bearing rocks. Alkalinity, represented by bicarbonate (HCO_3^-), and base cations including calcium (Ca^{2+}) and magnesium (Mg^{2+}) are common products of neutralization by these calcareous minerals. Where absent or deficient at a mine site, the addition of calcite, dolomite, or other alkalinity-producing materials to mine spoil or mine drainage can be effective for prevention or neutralization of AMD and the attenuation of metals transport.

Where reclamation of a mine or mining-related surface effects is not possible, treatment of AMD may be necessary to neutralize acidity and remove dissolved and suspended metals from the

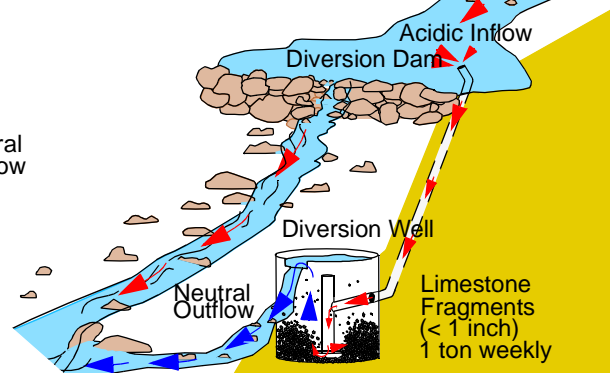
hydrologic system. Conventional treatment of acidic drainage involves the addition of strong alkaline chemicals to increase pH, which causes Fe, Al, Mn, and other metals to hydrolyze and precipitate (Skousen et al. 1998). Although effective, chemical treatment is expensive and funds to mitigate AMD are limited. Alternative treatment methods for AMD include wetlands and limestone-based systems (Hedin et al. 1994a; Skousen et al. 1998). These “passive systems” generally are limited by slower rates of neutralization and pollutant removal than for conventional treatments but can be cost effective where water chemistry meets suggested criteria and land and component materials are locally available (Skousen et al. 1998). Generally, if acidity exceeds alkalinity, limestone-based treatments could be appropriate to add alkalinity. If alkalinity exceeds acidity, oxidation ponds or aerobic wetlands are useful to remove metals as solids.

A variety of passive to semi-passive limestone treatment systems recently was installed at selected locations to neutralize the AMD and restore the aquatic ecosystem in approximately 25 mi (40 km) within the northern Swatara Creek watershed above Ravine, Pa. (figs. 1 and 2). The treatments, which include limestone-sand dosing, open limestone channels, anoxic and oxic limestone drains, limestone diversion wells, and limestone-based wetlands, were implemented mainly during fall 1996, spring 1997, and winter 1998 by the Schuylkill County Conservation District and the Northern Swatara Creek Watershed Association, with technical assistance from the U.S. Geological Survey (USGS) and the Pennsylvania Department of Environmental Protection (PaDEP). Additional treatments have been implemented since 1998 or are planned as funds can be obtained.

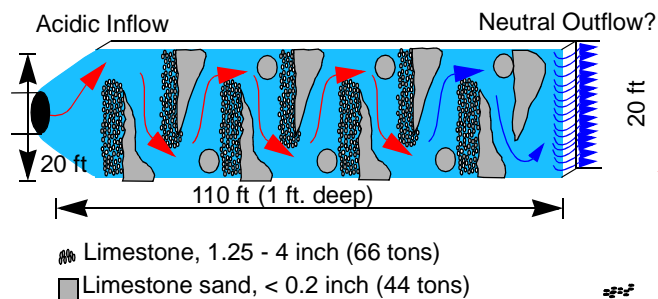
A. Anoxic/Oxic Limestone Drain



C. Limestone Diversion Well



B. Open Limestone Channel



D. Limestone-Compost Based Wetland

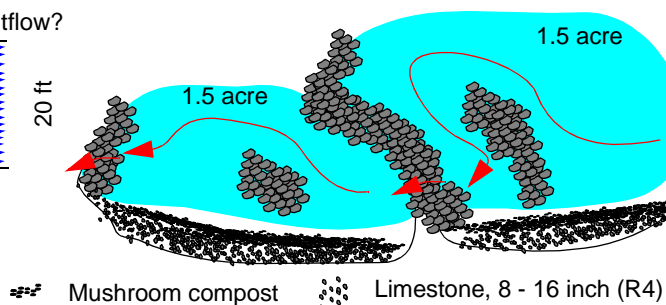


Figure 2. Schematic illustration of limestone treatment system designs: A, open limestone channel; B, limestone diversion well; C, limestone drain; D, limestone-compost wetland.

Open limestone channels and limestone-sand dosing generally are simple treatment systems where limestone is added directly to the stream channel (Ziemkiewicz et al. 1997; Skousen et al. 1998). An open limestone channel was constructed within a 110-ft (33.5 m) long segment of Swatara Creek at site B2 (fig. 1) on March 21, 1997. A total of 44 tons (40 Mg) of sand-size fragments (<0.2 inch; <0.5 cm) and 70 tons (63 Mg) of larger fragments (1.25-4 inches; 3-11 cm) were installed as a series of alternating berms extending part way across the 15-ft- (4.6-m) wide channel from opposite sides of the stream (fig. 2). Limestone sand, which can dissolve rapidly because of its small diameter, also was dumped into Coal Run (14 tons; 12.6 Mg) between sites C4 and C6 on September 4, 1996, and into Lorberry Creek (150 tons; 136 Mg) below site E2 on February 13-14, 1997 (fig. 1).

A limestone drain is another relatively simple treatment method that involves the burial of coarse limestone in air-tight trenches that intercept acidic discharge water (Hedin et al. 1994a, b; Skousen et al. 1998; Cravotta and Trahan 1999). Keeping carbon dioxide within the drain can enhance limestone dissolution and alkalinity production (Cravotta and Trahan 1999). Keeping O₂ out of contact with the discharge water minimizes the potential for oxidation of Fe²⁺ and the consequent precipitation of Fe(III) encrustation, or armoring, on the limestone surfaces, while allowing O₂ into the drain can promote oxidation and hydrolysis reactions and the removal of Fe, Mn, and trace metals (Cravotta and Trahan 1999). Limestone drains designed for varying flow rates and chemistry were constructed on March 15, 1995, at site E3-S0 to treat a small acidic discharge (10-30 gal/min (38-113 L/s), oxic inflow; 44 tons (40 Mg) limestone) along Lower Rausch Creek; on May 21, 1997, at site A1 to treat a large, anoxic discharge (50-200 gal/min (189-756 L/s); 400 tons (363 Mg) limestone) at the headwaters of Swatara Creek; and on June 22, 2000, at site C0 to treat a large oxic discharge (100-500 gal/min (378-1,890 L/s); 800 tons (727 Mg) limestone) near the headwaters of Swatara Creek (figs. 1 and 2). The design of the larger two systems was based on results for the smaller system where pH increased from 3.5 to 6.0-6.5 through the drain during 1-3 hour residence time (Cravotta and Trahan 1999).

In a limestone diversion well (fig. 2), acidic water is diverted from upstream points, and the hydraulic force of the piped flow is deflected upward through limestone fragments inside 4-ft (1.2-m) diameter "wells" (Arnold 1991). Approximately 0.5-1 ton of limestone is consumed weekly by each operating diversion well. Hydraulic churning abrades limestone to fine particles and prevents encrustation of the limestone by Fe(III) or Al oxyhydroxides. Dissolution of limestone within and downstream of the diversion wells promotes pH increases. In addition to pulverized limestone, Fe(III) and Al oxyhydroxides precipitate and accumulate downstream of the diversion wells. On November 14, 1995, a pair of diversion wells was installed to treat water diverted from Swatara Creek at site C2; on July 13, 1997, a single diversion well was installed to treat water from Martin Run at site C8; and on December 15, 1998 a pair of diversion wells was installed to treat water from Lorberry Creek above site E2-0 (fig. 1).

Constructed wetlands for treatment of mine drainage can attenuate the transport of dissolved and suspended pollutants by promoting the production of alkalinity and the precipitation and deposition of iron and other metals (Hedin et al. 1994a; Skousen et al. 1998). For net acidic water (acidity > alkalinity), wetlands that have compost and/or limestone substrates can be appropriate. The organic matter in the compost provides a substrate for plant rooting and for microbial reduction of SO₄. On December 1997, near the mouth of Lower Rausch Creek at site E3 (figs. 1, 2), a 3-acre (1.2 ha) compost-limestone based wetland was constructed to remove metals from streamflow that commonly had near-neutral pH but had potential to be net acidic if untreated

during stormflow conditions. The Lower Rausch Creek wetlands were constructed downstream from the outflow of the “oxic limestone drain” (OLD) built in 1995 (fig. 1). Although the OLD was effective for neutralizing acid and converting dissolved metals to solid forms as described in another report (Cravotta and Trahan 1999), a settling basin or wetland was needed to attenuate the transport of suspended metals from the OLD and other sites in the Lower Rausch Creek watershed.

In general, passive-treatment systems are designed to be effective for the typical baseflow water-quality conditions. Despite recent documentation of case studies for passive systems in the Northern Appalachian Region (Skousen et al. 1998), hydrological and geochemical factors affecting the performance of passive limestone-treatment systems are poorly characterized, particularly for high-flow conditions. Each treatment has different advantages and disadvantages; however, all suffer from possible complications associated with variability of flow rates and chemistry of the AMD-contaminated water and from uncertainties about efficiency and longevity of the treatment. Furthermore, every site requiring treatment has unique characteristics.

This paper characterizes site conditions and evaluates the effectiveness of limestone treatments for neutralizing acidity and removing metals and other pollutants from AMD and affected stream water in the Swatara Creek watershed. Data collected by USGS primarily during June 1996 through June 2000 for sites within the Swatara Creek watershed above Pine Grove, Pa., are used for this evaluation. Additionally, historical USGS data for Swatara Creek at Ravine, Pa., collected periodically since 1959 are used to indicate long-term trends in water quality.

Methods

To characterize untreated AMD, treatment-system performance, and cumulative downstream effects over a range of environmental conditions, the USGS established monitoring sites upstream and downstream of each treatment and along lower reaches of Swatara Creek (fig. 1). During base-flow and high-flow conditions in 1995-2000, data on streamflow rate and water quality were collected at these sites.

Three sites on Swatara Creek, site C3 near Newtown (station 0157155014), site D1 near Ravine (station 01571820), and site D2 near Pine Grove (station 01572025), were equipped with automatic stage-recording, water-quality monitoring, and (or) water-sampling devices in 1996. Automatic water-quality monitoring devices also were installed in 1996 at site C1 (station 0157155010) above site C3, and in 1999 at sites E2-244 (station 403542076263201), E2-0 (station 01571774), and E2-2 (station 01571778) on Lorberry Creek. Where equipped, stream stage was measured continuously with a pressure transducer; temperature, pH, and specific conductance (SC) were measured with a multiparameter sonde. The stage and water-quality data were recorded at 15-minute intervals with an electronic data logger. Continuous streamflow was computed on the basis of a stage-discharge rating developed for each site (Rantz et al. 1982a, b). At these and other sites, instantaneous data for temperature, SC, dissolved O₂ (DO) and pH also were measured when samples were collected or processed by use of calibrated instruments (Wilde et al. 1998).

At all sites, baseflow and stormflow samples were collected manually as grab samples from well-mixed zones in the stream or mine discharge. At sites equipped with automatic samplers (sites C3, D1, and D2), discrete stormflow samples were collected using pumping samplers containing

24 1-L polyethylene bottles. The automatic samplers were programmed to initiate sampling after a specified rise in stream stage above the current base stage and to proceed at intervals based on rate of change in stage until the stream returned to the base stage. Samples submitted for analysis were selected to cover rising, peak, and falling stages of the storm hydrograph. Stormflow samples were analyzed for more than 20 events, including significant storms in October and December 1996, May 1997, January 1998, January and September 1999, and May 2000 (fig. 3).

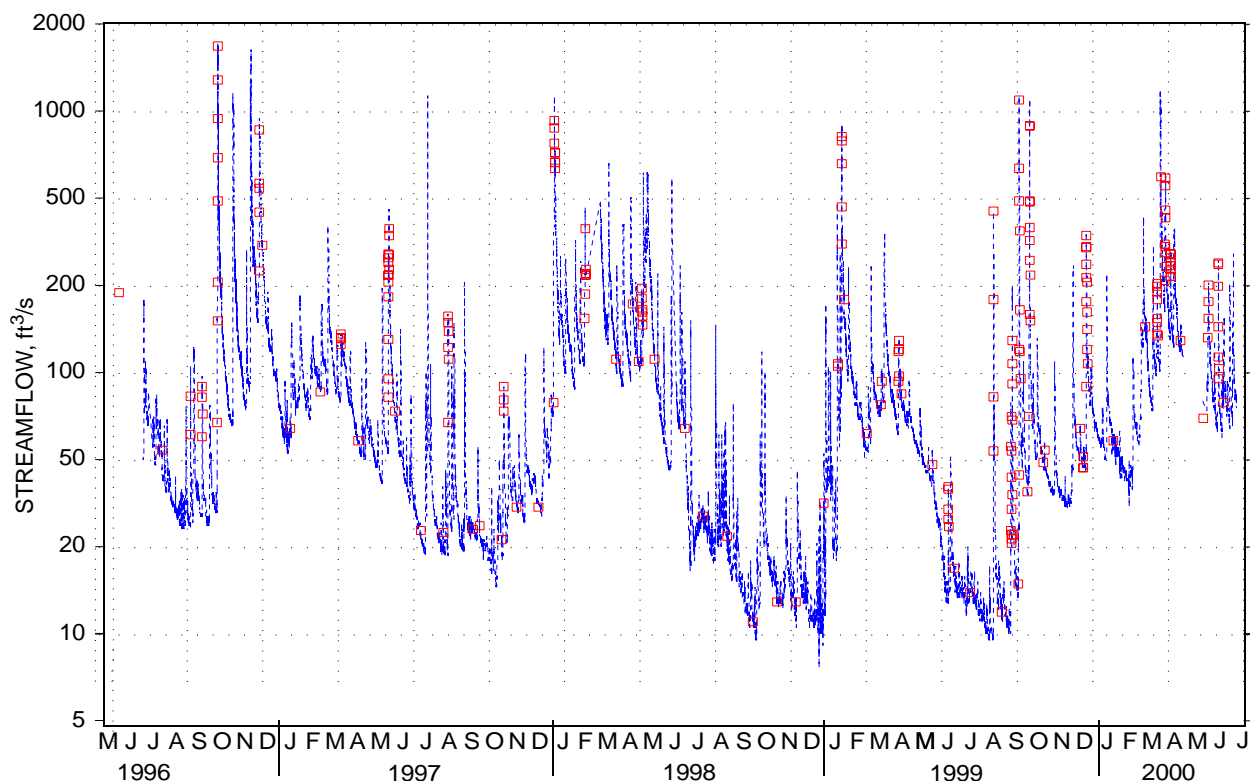


Figure 3. Streamflow hydrograph for Swatara Creek near Ravine, Pa., June 1996 - June 2000.
Square symbols indicate streamflow at times water-quality samples were collected.

Water samples were split into subsamples in the field or in the USGS laboratory in Lemoyne, Pa., and stored in sample-rinsed polyethylene bottles at 4°C until analyzed. Samples for dissolved (0.45- μ m filter) and total recoverable (whole-water; in-bottle nitric and hydrochloric acid digestion) metal analysis were stored in acid-rinsed polyethylene bottles and acidified with nitric acid (HNO₃). Samples were analyzed for major ions, metals, and nutrients by inductively coupled plasma optical emission spectroscopy (ICP-OES), ion chromatography (IC), colorimetry, and electrometric titration at the PaDEP Bureau of Laboratories facility in Harrisburg, Pa., following methods of Greenberg et al. (1992), Hoffman et al. (1996), and Fishman and Friedman (1989). Most unknown samples met ionic charge-balance criteria ($\pm 10\%$) and had dissolved concentrations less than, or equal to, total concentrations. Furthermore, duplicates, blanks, and standard reference samples that were submitted periodically with batches of unknown samples typically indicated precise and accurate measurements. The water-quality and streamflow data, which are maintained in the USGS National Water Information System (NWIS) data base, were published annually (Durlin and Schaffstall 1998, 1999, 2000).

Fish were collected annually at the Ravine site by electrofishing over a 500-ft (150-m) reach consisting of mixed riffle, run, and pool habitats as described by Bilger et al. (1999). Individual fish were collected with dip nets, identified, and measured before releasing most specimens. Some specimens were sacrificed for analysis of metals in fish tissue as reported by Cravotta and Bilger (2001).

Results and Discussion

Characterization of Stream-Water Quality Prior to Treatment

Historical and current data from 1959 to 2000 indicate progressive improvement in water quality for Swatara Creek at Ravine. Baseflow samples were collected for comparable streamflow conditions for the historical and current record. Baseflow SO_4 declined from a median of about 150 mg/L in 1959 to 75 mg/L in 1999; pH increased sharply from 3.5-4.4 (median ~4) to 4.6-7.0 (median ~6) after 1975 (fig. 4). The decline in SO_4 concentration probably was caused by a decline in pyrite oxidation after flooding of the abandoned mines had minimized inflows of oxygenated air and water. The associated increase in pH was caused by the onset of carbonate buffering which occurred when the rate of alkalinity production equalled or exceeded acid production (Cravotta et al. 1999). Although a variety of environmental factors could affect pH and SO_4 concentrations, consistently near-neutral pH values with variable SO_4 concentrations at Ravine during 1998-2000 (fig. 4) imply that the recently implemented limestone treatments have neutralized acid, further improving water quality.

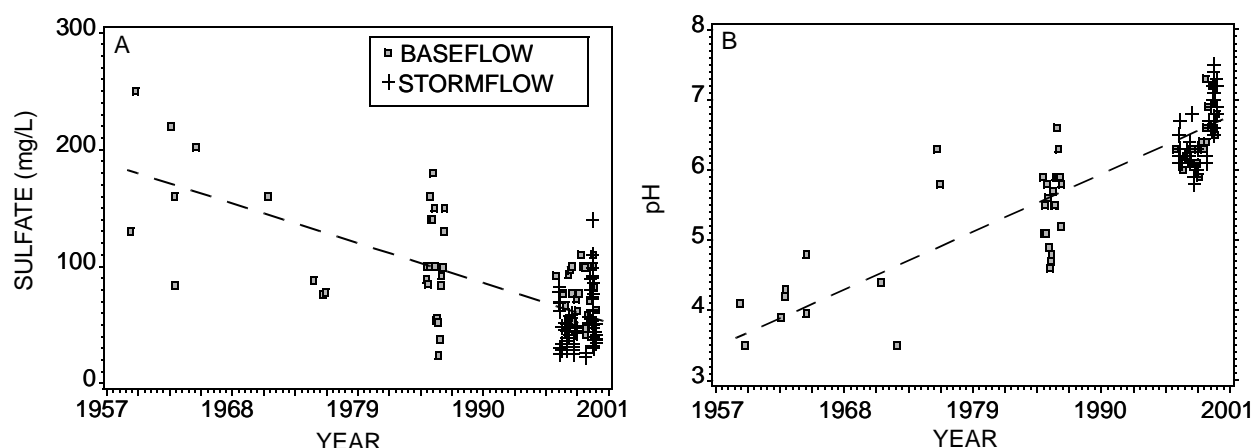


Figure 4. Long-term water-quality trends for Swatara Creek at Ravine, Pa.: A, Sulfate; B, pH. Data from McCarren et al. (1964), Stuart et al. (1967), Skelly & Loy, Inc. (1987), Fishel (1988), and Durlin and Schaffstall (1998, 1999, 2000).

As a consequence of the improved water quality, the fish community has rebounded (fig. 5). Fish were nonexistent in Swatara Creek at Ravine during ecological surveys prior to 1991 (fig. 5). However, in 1994 and 1996, six species of fish were found. Increasing numbers of fish species have been documented annually since 1996; 21 species were found in 1999 (fig. 5). A similar, though less dramatic increase in benthic macroinvertebrate species is also occurring. In 1995, no macroinvertebrates were found at Ravine; in 1999, 16 taxa were found (Cravotta and Bilger 2001).

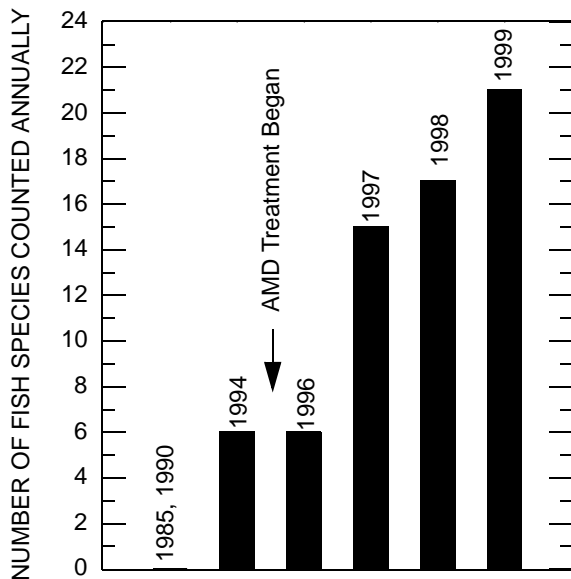


Figure 5. Recent trends in fish species abundance for Swatara Creek at Ravine, Pa. Year of survey indicated above bar; data from Cravotta and Bilger (2001).

During the 1996-2000 study period, stream water of Swatara Creek at Newtown (site C1 in fig. 1) and Ravine (site D1 in fig. 1) was mildly acidic to near-neutral (pH 4.5 - 8.0) with moderate concentrations of dissolved solids (SC 60 - 400 $\mu\text{S}/\text{cm}$). The pH, SC, and concentration of SO_4 were correlated and inversely related to streamflow (figs. 6, 7A). Higher values of pH, SC, and SO_4 were associated with baseflow conditions sustained by near-neutral AMD in the watershed, such as the Tracy Airhole, Colket, and Marshfield discharges (Durlin and Schaffstall 1998, 1999, 2000). Lower values of pH, SC, and SO_4 were associated with stormflow (Cravotta 2000; Cravotta and Bilger 2001). Mixing of baseflow with acidic rainfall and storm runoff having low pH and low dissolved solids explains the major stormflow characteristics of declining pH, SC, and SO_4 with increased streamflow for these reaches of Swatara Creek (Cravotta 2000).I

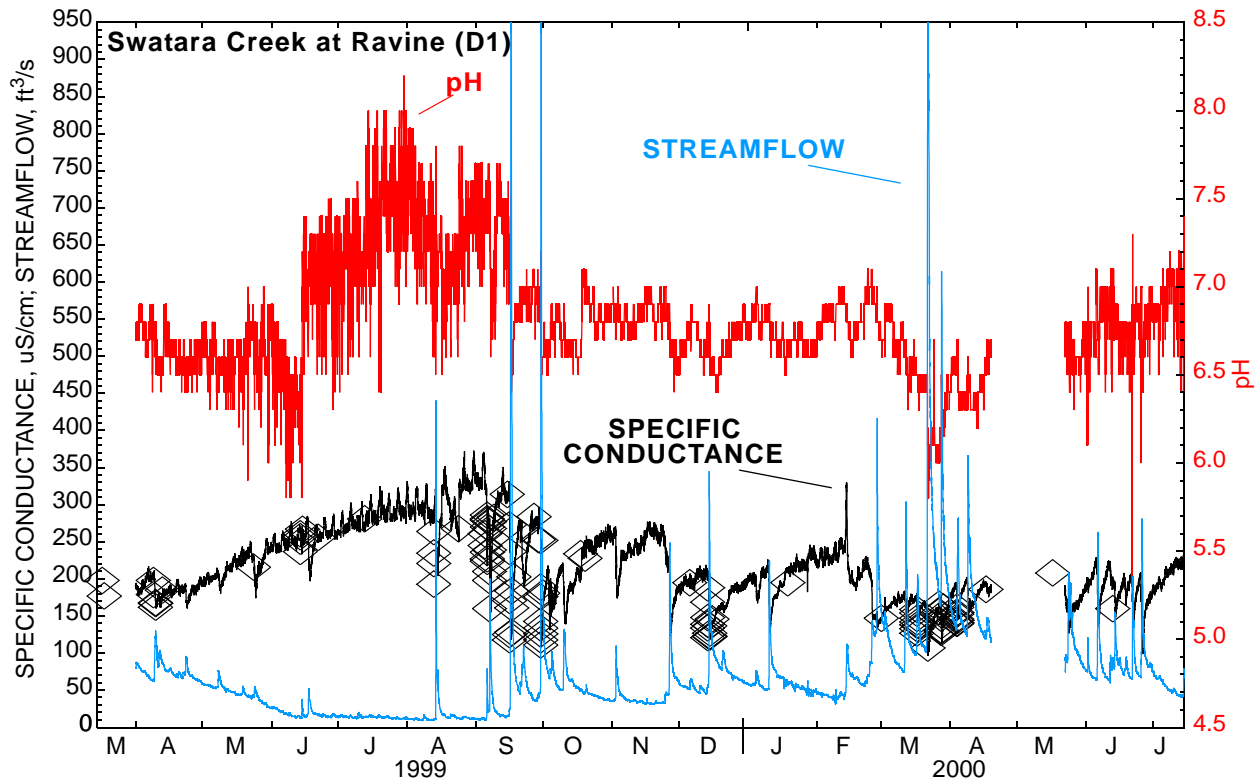


Figure 6. Continuous data for streamflow, specific conductance (SC), and pH, Swatara Creek at Ravine, Pa., March 1999 - July 2000. Black diamonds indicate SC of automatically or manually collected grab samples.

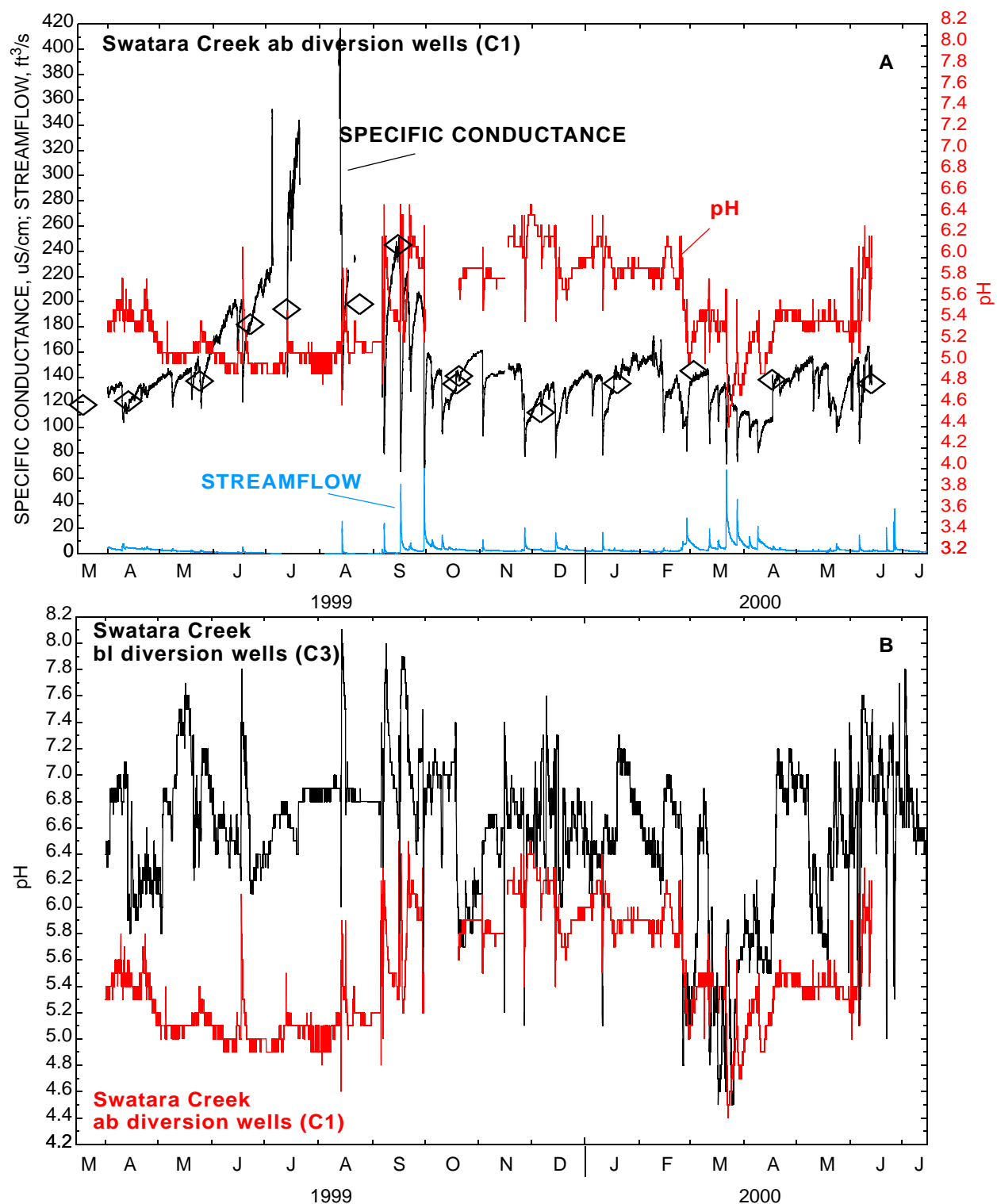


Figure 7. Continuous data for streamflow, SC, and pH, Swatara Creek at Newtown, Pa., March 1999 - July 2000: A, Streamflow, pH, and SC, upstream of diversion wells (black diamonds indicate SC of manually collected grab samples); B, pH upstream and downstream of diversion wells.

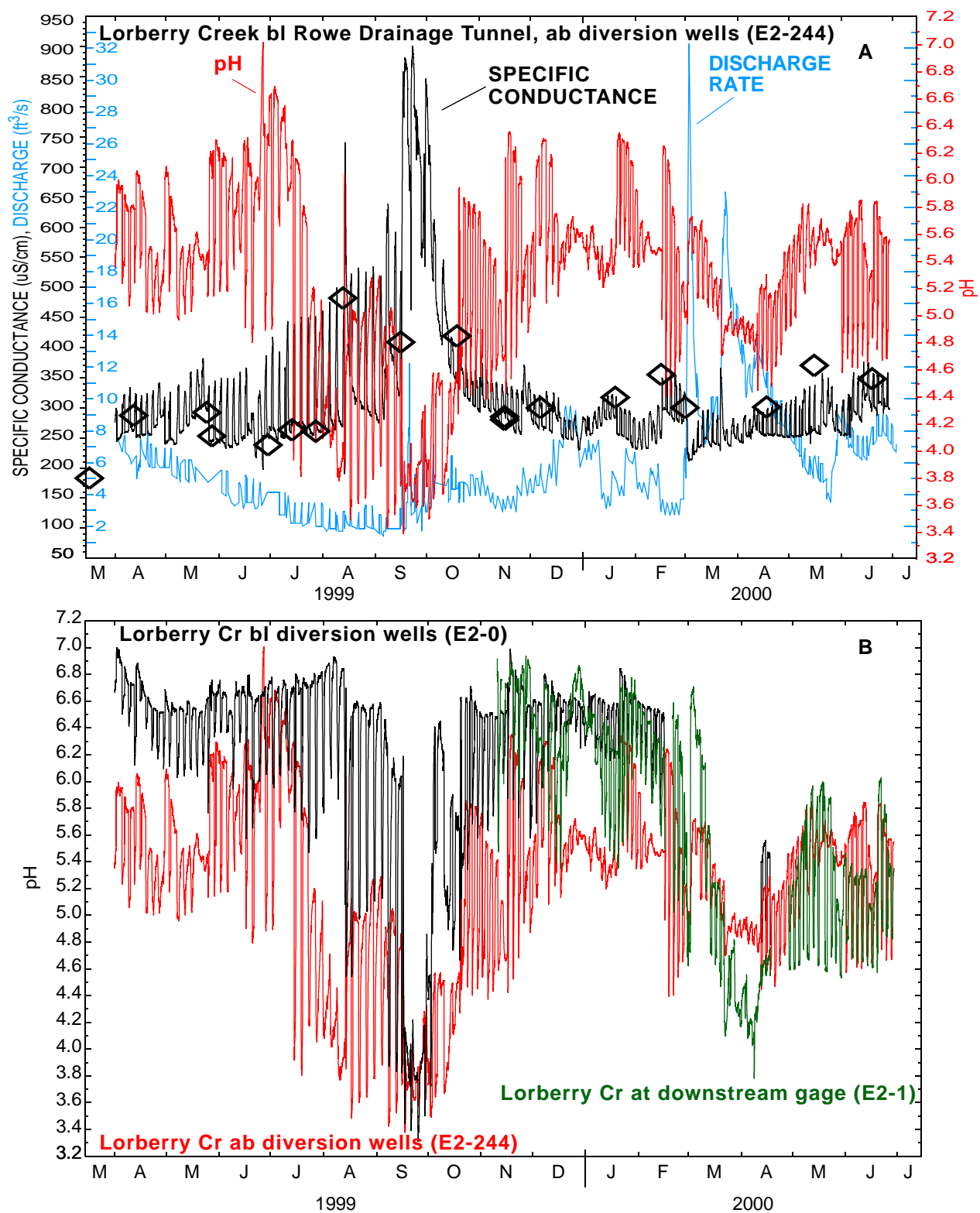


Figure 8. Continuous data for SC and pH, Lorberry Creek above Lorberry Junction, Pa., March 1999 - July 2000: A, pH and SC, upstream of diversion wells (black diamonds indicate SC of manually collected grab samples); B, pH upstream and downstream of diversion wells.

In contrast with data for Swatara Creek at Newtown and Ravine, the pH and SC for headwaters of Lorberry Creek, below the Rowe Drainage Tunnel (site E2-244 in fig. 1), were inversely correlated and varied more widely than those for Swatara Creek sites (fig. 8A). Decreased pH and increased SC resulted from additions of acidic water containing elevated concentrations of SO_4 and other dissolved ions. Two processes contributed to the temporal fluctuations in pH and SC of Lorberry Creek. Although the Rowe Drainage Tunnel drains the abandoned, flooded New Lincoln Colliery complex, an underground mine that is currently active below the complex periodically pumps untreated, acidic water to the New Lincoln mine pool. On the shorter scale of a few days, periodic fluctuations in pH and SC result from the addition of this untreated AMD to the water drained from the abandoned mine complex. When the pumping was active, pH of Lorberry Creek declined by 0.5 to 1 unit while SC increased 50 to 200 $\mu\text{S}/\text{cm}$. These short-term fluctuations in pH and SC were apparent for the continuous monitoring data but generally were not captured in the data for monthly grab samples (fig. 8A). On the broader time scale, pH declined and SC increased during a drought from May through August 1999 followed by two tropical storms in September 1999. Prior to this investigation, the Rowe Drainage Tunnel was characterized as near-neutral to moderately acidic AMD (pH 5-6; SC <400 $\mu\text{S}/\text{cm}$) requiring only the removal of particulate iron. As illustrated by the continuous monitoring data, however, the mine discharge was extremely acidic for sustained periods lasting hours to weeks (pH 3-4; SC 500-950 $\mu\text{S}/\text{cm}$) during 1999-2000.

Declines in stream-water pH to values approaching 5.0, as for extreme events during 1996-2000, could cause injury to aquatic organisms (e.g. Baker and Schofield 1982; Earle and Callaghan 1998) and could result in the remobilization of adsorbed or precipitated metals associated with streambed sediments (e.g. Francis et al. 1989). Solid forms of the metals, as particulate and particle coatings, can be transported during storms and ingested and accumulated by aquatic organisms (e.g. Elder 1988; Cravotta and Bilger 2001). Hence, pH adjustment as well as removal of metals from the hydrologic system would be needed to meet water-quality goals.

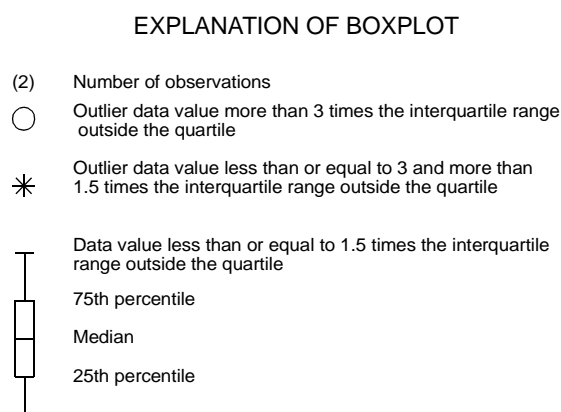


Figure 9A. Boxplots of pre- and post-implementation water-quality data for grab samples upstream and downstream of selected treatment systems in Swatara Creek Basin. Explanation, only (boxplots showing data follow).

Evaluation of Treatment Effects

The pretreatment and post-treatment data for pH, net alkalinity (alkalinity - acidity), dissolved iron, and dissolved aluminum at sites upstream and downstream of six different treatment systems in the Swatara Creek watershed are illustrated as boxplots (fig. 9). The boxplots show data for all samples. Table 1 indicates results of tests for difference between paired samples (same date) from the upstream and downstream sites. Differences between the pairs were evaluated for the range of flow and for low-, normal-, and high-flow classes. If streamflow at Ravine on the date of sampling was less than the 25th percentile for the study period, the sample was classified "low-flow"; between the 25th and 75th percentiles, the sample was classified "normal-flow"; or greater than the 75th percentile, the sample was classified "high-flow" (fig. 10).

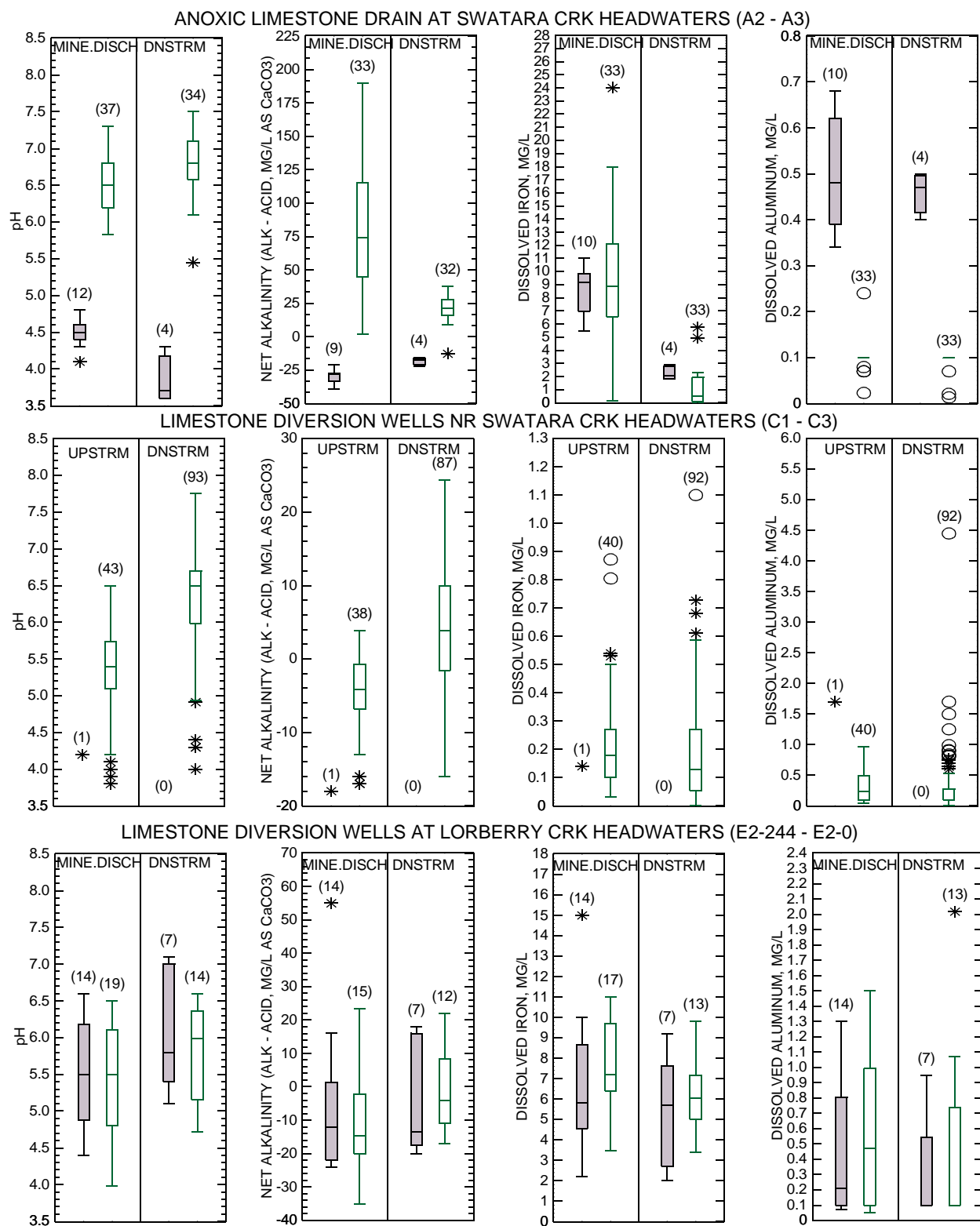


Figure 9B. Boxplots of pre- and post-implementation water-quality data for grab samples upstream and downstream of selected treatment systems in Swatara Creek Basin. Pre-implementation data shaded. See explanation of boxplot in figure 10A.

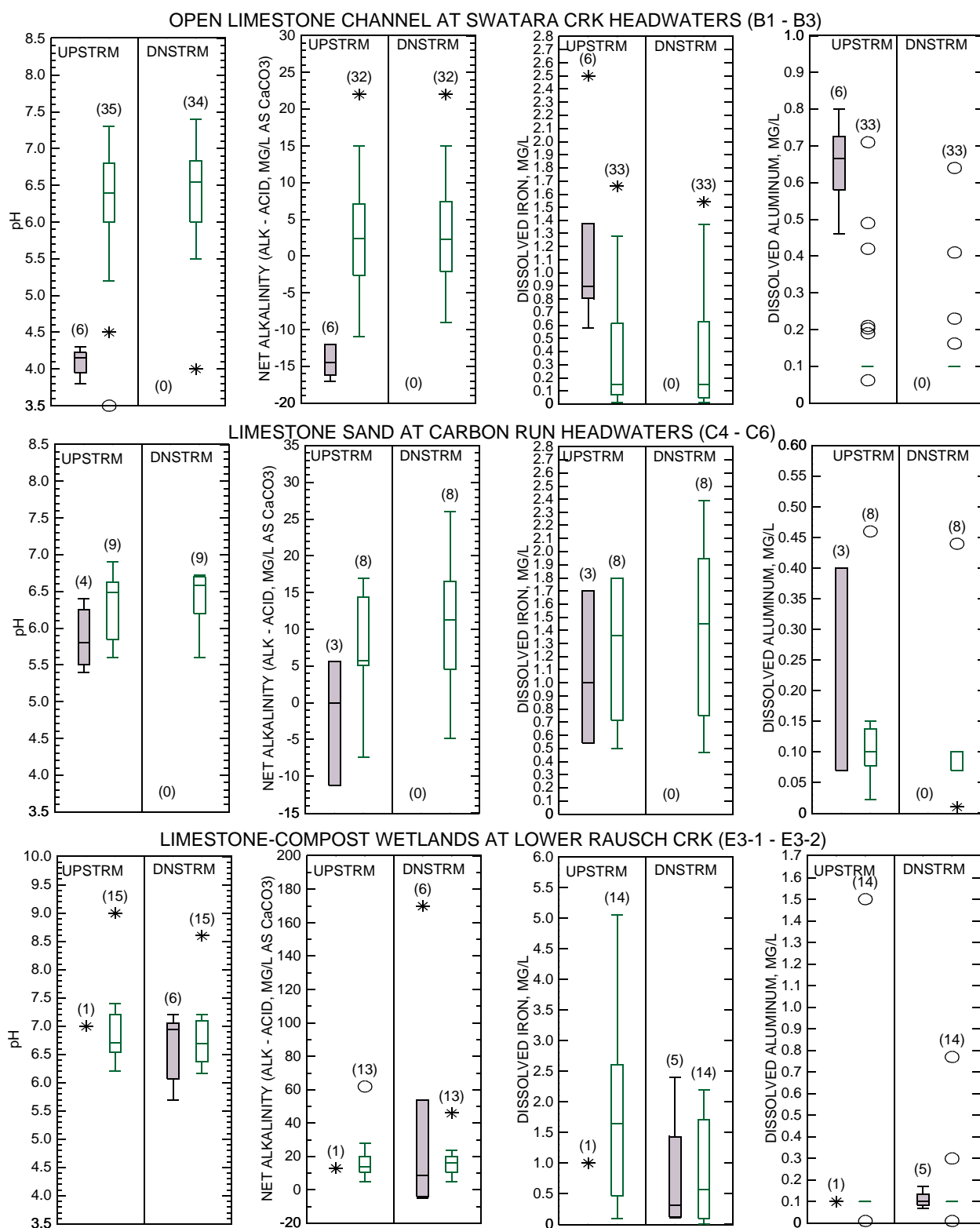


Figure 9C. Boxplots of pre- and post-implementation water-quality data for grab samples upstream and downstream of selected treatment systems in Swatara Creek Basin. Pre-implementation data shaded. See explanation of boxplot in figure 10A.

Table 1. Probability (p-value¹) that concentration or transport of constituents at downflow monitoring site is the same as that from the upstream monitoring site over a range of hydrologic conditions, June 1996 - July 2000
[For p-values less than 0.1, ">" or "<" indicates mean rank at downflow site was greater than or less than that for the upstream site, respectively; n.p., p-value not computed]

Hydrologic Condition ²	Streamflow Rate	Temperature	Specific Conduct.	pH	Net Alkalinity (ALD) implemented May 21, 1997 near Swatara Creek Headwaters (A2 - A3)	Calcium Dissolved	Sulfate Dissolved	Iron Dissolved	Aluminum Dissolved	Manganese Dissolved	Suspended Solids
Anoxic Limestone Drain (ALD) implemented May 21, 1997 near Swatara Creek Headwaters (A2 - A3)											
All samples, n=30	0.00 (>)	0.82	0.00 (<)	0.00 (>)	0.00 (<)	0.00 (<)	0.24	0.00 (<)	1.00	0.00 (<)	0.16
Low, n=8	0.09 (>)	.40	0.00 (<)	.93	0.00 (<)	0.03 (<)	0.00 (>)	0.02 (<)	n.p.	.33	.02 (<)
Normal, n=12	0.01 (>)	.64	0.01 (<)	0.01 (>)	0.00 (<)	0.00 (<)	.12	0.00 (<)	1.00	.00 (<)	.03 (<)
High, n=10	0.01 (>)	.88	0.00 (<)	0.00 (>)	0.00 (<)	0.00 (<)	0.00 (<)	0.00 (<)	n.p.	.00 (<)	.36
Open Limestone Channel (OLC) implemented March 21, 1997 near Swatara Creek Headwaters (B1 - B3)											
All samples, n=33	1.00	0.00 (>)	0.00 (>)	.47	.14	.12	.03 (<)	.33	.09 (>)	.04 (<)	.29
Low, n=9	1.00	1.00	0.02 (>)	.73	1.00	.84	n.p. (<)	1.00	.78	.00 (<)	1.00
Normal, n=14	1.00	.33	0.06 (>)	.58	.35	.48	.40	.97	.06 (>)	.04 (<)	.44
High, n=10	1.00	1.00	.50	0.00 (>)	.21	.12	.22	.17	.37	.14	.94
Limestone Sand (LSC) implemented September 4, 1996 near Coal Run Headwaters (C4 - C6)											
All samples, n=16	1.00	1.00	0.08 (>)	.26	.09 (>)	.00 (>)	.50	.21	.14	.05 (>)	.11
Low, n=2	1.00	n.p.	n.p.	n.p.	n.p.	n.p.	n.p.	n.p.	n.p.	n.p.	n.p.
Normal, n=10	1.00	.22	0.05 (>)	.60	.27	.00 (>)	.22	.27	1.00	.00 (>)	1.00
High, n=4	1.00	1.00	.65	n.p.	n.p. (>)	n.p.	n.p. (<)	n.p.	n.p. (<)	n.p. (<)	n.p.
Limestone Diversion Wells (LDZ) implemented November 11, 1995 near Swatara Creek Headwaters (C1 - C3)											
All samples, n=40	1.00	.60	0.00 (>)	0.00 (>)	0.00 (>)	0.00 (>)	.22	0.00 (<)	0.00 (<)	.69	.83
Low, n=11	1.00	.92	0.04 (>)	0.00 (>)	0.00 (>)	0.00 (>)	.40	0.01 (<)	0.00 (<)	.11	.04 (<)
Normal, n=18	1.00	.28	0.02 (>)	0.00 (>)	0.00 (>)	0.00 (>)	.04 (>)	0.00 (<)	.02 (<)	.06 (>)	.23
High, n=11	1.00	.95	0.03 (>)	0.00 (>)	0.00 (>)	0.00 (>)	.67	.20	1.00	.44	.10 (>)
Limestone Diversion Wells (LDL) implemented November 19, 1998 near Lorberry Creek Headwaters (E2-244 - E2-0)											
All samples, n=13	1.00	.61	0.01 (<)	0.00 (>)	.01 (>)	.29	.01 (<)	0.00 (<)	0.06 (<)	.03 (<)	.01 (<)
Low, n=2	1.00	n.p.	0.00 (>)	0.00 (>)	.65	0.00 (>)	n.p.	0.00 (<)	n.p.	.00 (<)	n.p.
Normal, n=6	1.00	.28	.17	0.00 (>)	0.00 (>)	.42	.11	.35	.68	.21	.18
High, n=5	1.00	.75	0.06 (<)	0.05 (>)	.14	.86	0.00 (<)	0.00 (<)	.14	n.p. (<)	.00 (<)
Limestone-Compost Base Wetlands (WLR) implemented December 15, 1998 at mouth of Lower Rausch Creek (E3-1 - E3-2)											
All samples, n=13	0.01 (<)	.24	.98	.18	.64	.53	.13	0.00 (<)	.02 (<)	.03 (<)	.01 (<)
Low, n=2	0.01 (<)	0.00 (>)	0.00 (>)	n.p.	n.p.	n.p.	n.p.	0.00 (<)	0.00 (<)	.00 (<)	n.p.
Normal, n=6	.50	.67	.13	0.00 (<)	.36	.60	.22	.03 (<)	.46	.11	.08 (<)
High, n=5	0.04 (<)	.92	.35	.60	.86	.35	n.p.	.08 (<)	.00 (<)	.46	.00 (<)

¹The p-value is the two-tailed probability that constituent values for the matched pairs of upstream and downstream samples are the same on the basis of the Wilcoxon matched-pair signed-rank test (P-STAT, Inc. 1989; Helsel and Hirsch 1992). For each pair, the constituent value for the upstream site was subtracted from that for the downstream site. The null hypothesis, H₀, is that the median of the difference ranks is zero. The smaller the p-value, the stronger the evidence for rejection of H₀. If a p-value was not computed, the p-value is shown as 1.0 if ties > 2/3 total count and all differences are <0 or >0 or it is shown as n.p. with trend if ties < 2/3 total count and all differences are <0 or >0.

²Hydrologic condition for date of sampling at reference site on Swatara Creek at Ravine, Pa. Low-, normal-, and high-flow conditions for less than 25th, 25th to 75th, and greater than 75th percentile values, respectively, of mean-daily flow frequency distribution for the period June 1996 - July 2000 (see figure 10).

³See figure 1 for location of sites and text for description and discussion of treatment.

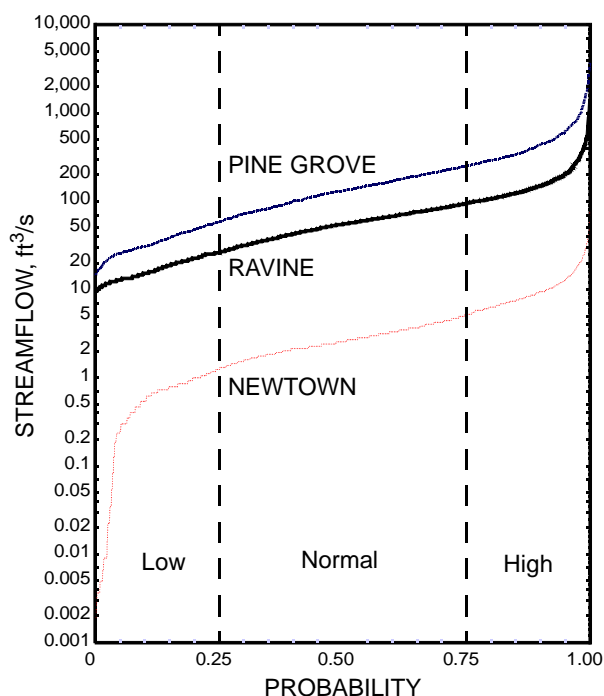


Figure 10. Probability of streamflow for Swatara Creek at Newtown, Ravine, and Pine Grove, Pa., June 1996 - July 2000. Vertical lines at 25th and 75th percentiles divide “low”, “normal”, and “high” flow intervals.

Anoxic Limestone Drain (A2 - A3). Before construction of the anoxic limestone drain (ALD) at site A2 near the headwaters of Swatara Creek, acidic mine drainage flowed from site A2 for about 600 yd (550 m) to site A3 at Swatara Creek (fig. 1). The untreated AMD was anoxic ($\text{DO} < 0.5 \text{ mg/L}$) and had elevated concentrations of dissolved Fe and Al (fig. 9B). As this water became aerated flowing downstream from sites A2 to A3, the pH and Fe concentrations declined due to oxidation and hydrolysis of Fe (reactions 2 and 3); however, dissolved Al remained elevated ($> 0.3 \text{ mg/L}$) because of low pH (< 4). After construction of the ALD, the concentration of dissolved Fe was unchanged at the ALD outflow compared to the untreated mine discharge, whereas the pH and net alkalinity increased and dissolved Al concentration decreased ($< 0.1 \text{ mg/L}$) (fig. 9B; mine discharge, pre- vs. post-implementation). As the treated water flowed downstream from sites A2 to A3, the pH increased while the net alkalinity and Fe concentrations decreased due to aeration and the resulting exsolution of carbon dioxide and oxidation and hydrolysis of Fe. The result was significantly improved, near-neutral water quality at site A3. Even

though high flows diluted the effects at the downstream site(s), the ALD treatment was effective for neutralization of AMD and attenuation of metals over the range of flow conditions (table 1).

Open Limestone Channel (B1 - B3). Before construction of the open limestone channel (OLC) near the headwaters of Swatara Creek, the stream water at sites B1 and B3 was acidic, with pH < 4.5 but relatively low concentrations of Al and Fe ($0.5\text{--}3 \text{ mg/L}$) for a mining-affected stream (fig. 9C). These conditions and preliminary field experiments indicating initially rapid increases in the pH of stream water in contact with limestone warranted the construction of the OLC. The preliminary experiments indicated the rate of limestone dissolution decreased with increased pH, which is consistent with other reports (e.g. Cravotta and Trahan 1999). However, the conditions of preliminary testing at the OLC were reflected for only one set of post-implementation samples before the ALD was constructed on an upstream tributary. The ALD, which was constructed 2 months after the OLC was constructed, produced near-neutral stream water at site B1 above the OLC (fig. 9C; upstream, pre- vs. post-implementation). This near-neutral water was not aggressive toward limestone in the stream channel compared to acidic stream water. Hence, differences in pH and concentrations of net alkalinity, and dissolved Fe and Ca between the upstream site (B1) and downstream site (B3) at the OLC were not significant for most flow conditions (table 1, fig. 9C). Nevertheless, decreases in concentrations of dissolved SO_4 , Al, and Mn were significant for some conditions (table 1).

Limestone Diversion Wells (C1 - C3). Before installation of the limestone diversion wells near the headwaters of Swatara Creek (LDZ), the stream water at sites C1 and C3 had pH <4.5 and dissolved Al >1.5 mg/L (fig. 9B). After installation, the pH of stream water at site C3 150 yd (137 m) below the diversion wells usually was 1-2 units higher than that at site C1 150 yd (137 m) above the wells (figs. 7B, 10B). Considering intermittent data, only, the limestone diversion wells increased pH, net alkalinity, and calcium for all flow conditions and decreased iron and aluminum at low- to normal-flow conditions. (fig. 9B). However, during extreme stormflow conditions associated with tropical storms in September 1999 and spring storms in March-May 2000, the pH of downstream water (continuously monitored) was not effectively increased (fig. 7B). During such stormflow conditions, the effectiveness of the limestone diversion wells was diminished because a smaller proportion of total streamflow was treated and metallic deposits from the streambed could be resuspended and (or redissolved). Additional or larger diversion wells would be needed to treat these large stormflows.

Limestone Diversion Wells (E2-244 - E2-0). Before installation of the limestone diversion wells below Rowe Drainage Tunnel (LDL), Lorberry Creek at sites E2-244 and E2-0 had variable pH (4-7), but typically was net acidic (median net alkalinity = -13 mg/L) and had high concentrations of Fe (median Fe = 5.8 mg/L) and Al (median Al = 0.2 mg/L) (fig. 9B). The diversion wells below Rowe Drainage Tunnel (LDL) increased pH and net alkalinity and decreased dissolved Fe and Al concentrations over variable flow conditions (fig. 9B, table 1). Nevertheless, the continuous monitoring data indicated that pH was not effectively changed during extremely high flow associated with tropical-storm conditions, probably because only a small proportion of total streamflow was treated. For the period March 1999 - July 2000, the pH of stream water at site E2-0 about 300 yd (274 m) below the diversion wells usually was higher than that for site E2-244 about 300 yd (274 m) above the wells (fig. 8B). During baseflow conditions through August 1999, the diversion wells effectively increased pH in the reach below the wells by about 1-2 units. However, during stormflow conditions associated with tropical storms in September 1999 and spring storms in March-May 2000, the pH of downstream water was not effectively increased. Additional or larger diversion wells would be needed to treat these large stormflows.

Limestone-Sand Dosing (C4 - C6). The limestone-sand dosing at Coal Run (LSC) was aptly called dumping, whereby several truck loads of sand were spilled over the bank into the channel. As the mound was eroded at the base, sand spilled into the channel. Although slight increases in net alkalinity and dissolved Ca concentrations were indicated by the matched-pair tests (table 1), the pH and metals concentrations were not different between the upstream site (C4) and downstream sites (C6) for most conditions (fig. 9C, table 1).

Limestone-Compost-Based Wetlands (E3-1 - E3-2). The wetlands at Lower Rausch Creek (WLR) did not affect pH, net alkalinity, Ca, or SO₄ concentrations, but were effective decreasing dissolved and total Fe and Mn and total Al over most flow conditions (fig. 9C, table 1). The implication is that the wetlands acted more as settling basins than as neutralization treatment systems. Although most pairs of samples indicated declines in metal concentrations and transport from the upstream to downstream monitoring sites, three pairs collected during different stormflow conditions indicated concentrations of total metals and suspended solids were greater at the downstream site than the upstream site.

Summary and Conclusions

Monitoring on the mainstem of Swatara Creek indicates watershed-scale effects owing primarily to changes in mining practices and secondarily to watershed-wide implementation of treatment systems. For Swatara Creek at Ravine, Pa., long-term data collected since 1959 indicate SO_4 concentration declined from about 150 mg/L in 1959 to 75 mg/L in 1999; pH increased sharply from 3.5-4.4 (median ~4) to 4.6-7.0 (median ~6) after 1975. These trends resulted from a decline in pyrite oxidation because of mine flooding and the onset of carbonate buffering attributed to natural processes (carbonate dissolution, SO_4 reduction) and recently installed limestone treatment systems.

A variety of limestone treatment systems were implemented during 1995-98 for the neutralization of acidity and the removal of dissolved metals in Swatara Creek and its tributaries. Continuous measurements of pH and SC and periodic sampling for chemical constituents upstream and downstream of each treatment system show that (1) the open limestone channel and limestone-sand dosing generally had negligible effects on water quality and (2) limestone diversion wells, limestone drains, and limestone-compost based wetlands generally were effective at attenuating dissolved and suspended metals during baseflow conditions but were less effective during stormflow conditions. Generally, stormflow tends to be acidic, and, as streamflow volume increases, a smaller fraction of total flow is treated and (or) residence time in the treatment system is reduced. Furthermore, metal-rich sediments commonly can be scoured and resuspended from the streambed during stormflow conditions.

Despite the implementation of a variety of limestone treatment systems during 1996-98 for the neutralization of acidity and the removal of dissolved metals, acidification of streamflow in the Swatara Creek Basin persisted locally and periodically, particularly during extreme hydrologic conditions associated with stormflow or drought conditions. Concentration of SO_4 , SC, and pH for Swatara Creek were correlated and generally declined with increasing streamflow at Newtown and Ravine, indicating episodic acidification and dilution from acidic rainfall and runoff during stormflow. In contrast, SC and pH were inversely correlated at Lorberry Creek, achieving lowest and highest values, respectively, during the drought of July-August 1999 and tropical-storm period of September 1999. During the drought and subsequent high-flow conditions in 1999, the Rowe Drainage Tunnel discharge changed from near-neutral (pH 5-6; SC <400 $\mu\text{S}/\text{cm}$) to acidic (pH 3-4; SC 500-950 $\mu\text{S}/\text{cm}$) causing acidification of Lorberry Creek to its mouth on Swatara Creek. Acidification of the mine discharge probably resulted from a decline in the water table, oxidation of previously inundated pyritic material, and subsequent dissolution of oxidation products by infiltrating water or as the water table rebounded. Nevertheless, the pH of Swatara Creek at Ravine remained near-neutral during this particular event.

The recent monitoring on the tributaries and mainstem of Swatara Creek indicates the limestone diversion wells and limestone drains mitigated extreme fluctuations in pH during most storm events; however, additional buffering capacity could be needed to maintain near-neutral pH of Swatara Creek for the extreme range of conditions. Generally, to maintain stream pH during storms, additional or larger limestone diversion wells could be constructed to begin or increase alkalinity production as the stream stage rises and/or additional or larger limestone drains could be constructed to produce greater amounts of alkalinity and enhance the buffering capacity of baseflow. Increasing the buffering capacity of baseflow also will mitigate acidification effects during drought conditions. Neutralization and pH buffering alone will not remedy the problem of

metals transport. Alkalinity-producing systems such as limestone diversion wells or limestone drains combined with wetlands could attenuate metals transport.

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